

DATA EVALUATION RECORD

Chemical Code 129057

STUDY 1

CHEM "Silver-Copper Zeolite"

FORMULATION: Pure active ingredient

Harris, J.C. 1990. Release of Silver and Copper under Hydrolysis Conditions.
Performed by Arthur D. Little, Inc., Cambridge, MA; Study #ADL 63614-02;
Completed 8/3/90. Submitted by Kanebo Zeolite USA, Inc., NY.
MRID #41613816

41615816

REVIEWED BY: S.C. Termes, Chemist
Review Section #3
OPP/EFED/EFGBW
(703) 305-5243

August 18, 1993

CONCLUSIONS

a. Administrative

The study provides only ANCILLARY (i.e, SUPPLEMENTAL) information at this time. The data presented do not address the release of Ag and Cu beyond 15-days, even though a very substantial release was observed at the day-15 sampling. Data beyond 15-days are required. This study is not a hydrolysis study, but a "release-from-the matrix" study at pHs 5, 7 and 9.

The registrant must clarify if the non-exchanged zeolite (that is, without exchange by Ag and Cu) would always be the same. If the registrant uses a variety of zeolites for exchange with Ag and Cu, characterization of the exchanged product and a 161-1 study for each different product may be required. The present study was conducted with a material provided by the registrant, which contains 3.4% Ag and 6.1% Cu by weight (anhydrous) and the results apply specifically to that product. In addition, the registrant must clarify the oxidation state of silver and copper in the parent "Ag-Cu Zeolite".

No attempts were made by the registrant to present the predominance of different Ag and Cu species that would be expected at the released concentrations at pH 5, at pH 7 and pH 9. The registrant must present data on concentration of Ag and Cu in the buffer systems and from the data estimate the predominance of Ag and Cu species at each of the three pHs. The same applies for the positive control ("spiked") samples. The registrant may choose a computer program such as MINTEQA to generate the data, indicating which species are soluble and which one are insoluble phases. Results should be compared to speciation of Ag and Cu as a function of pH in the absence of buffers.

OUTDOOR USES (Potential future use):

Since the use of buffers does not provide a realistic scenario for the release of Ag and Cu from "Ag-Cu Zeolite" in the environment (soil; natural waters),

the registrant can generate release rate data that more realistically approach environmental conditions. The Branch believes that the data obtained from this approach can be used towards supporting OUTDOOR uses. The suggested approach is to incorporate into the hydrolysate metal ions that are ubiquitous in soils and natural waters and that could exchange for Ag and/or Cu in the zeolite. The studies should be conducted in the absence of a buffer system and the following pH ranges are suggested 5 to 6; 6 to 7; 8 to 9. The cations to be used are Ca^{2+} (pH 6-7; pH 8-9) and Al^{3+} (pH 6-6) introduced in the aqueous system as the chlorides. For calcium at pH 8-9, the calcium ion activity should be below the solubility of the solid phase calcite (calcium carbonate); the aluminum ion activity would be determined by the solubility of gibbsite (aluminum hydroxide).

b. Scientific

According to the presented data, maximum release of Ag and Cu appears to occur at pH 5, with releases decreasing with increasing pH. There was a plateau at all pHs between 2 to 8 days, with a substantial release in the 15 day samples. However, since no sampling occurred beyond 15 days, the data do not provide any information on long-term release.

The studies were conducted in buffered systems at 25 C. Results reported by the registrant appear under the "REPORTED RESULTS" section.

MATERIALS AND METHODS

Test Material: The test material "Ag-Cu Zeolite" was provided by the sponsor. It contained 3.4% Ag and 6.1% Cu by weight (anhydrous). The moisture content was measured at the performing laboratory as 20.7%. No further physical-chemical characterization (except physical state and color) were reported.

Test System: The test system(s) consisted of 40-mL amber glass vials fitted with screw caps and Teflon-faced septa.

Each vial contained 30-45 mg sample of the "Ag-Cu Zeolite" and 30 mL of the desired buffer system (pH 5= acetate buffer; pH 7= phosphate buffer; pH 9= borate buffer). The ratio of buffer to zeolite was about 1 mL/mg.

Vials were placed in a temperature controlled chamber (25 ± 1 C) and protected from light. Samples were agitated by magnetic stirring.

The initial pH of the hydrolysis medium was measured by pH paper.

Control Samples: Negative (neat buffer solutions) and positive (buffer with standard solution of Ag^+ and Cu^{2+} at 25 ppb and 100 ppb, respectively) controls were used.

Sampling Time: 0, 1, 2, 4, 8, and 15 days.

Analytical Methodology: After removal from vial, hydrolysates were passed through 0.45 ug Teflon filters to ensure that only dissolved silver and copper were measured; filtrates were stabilized with nitric acid and stored at 4 C prior to analysis.

Hydrolysates and negative and positive standards were analyzed by Inductively Coupled Argon Plasma (ICAP). Calibration curves and calculated sample concentrations were based on the average area of the ICP signal for 4-sequential aspirations of each solution.

All release rate data was corrected to unit weight of zeolite powder,

$$\text{ug/mL} = \frac{\text{ppb(ug/L)} \times 0.030\text{L (hydrolysate volume)}}{\text{weight of zeolite present}}$$

REPORTED RESULTS:

The release rate of Ag and Cu from "Ag-Cu Zeolite" in buffered systems at pH 5, 7 and 9 are summarized below,

	<u>pH 5</u>		<u>pH 7</u>		<u>pH 9</u>	
	<u>Ag</u>	<u>Cu</u>	<u>Ag</u>	<u>Cu</u>	<u>Ag</u>	<u>Cu</u>
Release Rate (ug/mg zeolite/day)	0.59	0.49	0.047	0.15	0.023	0.051
% of Total Metal after 15 days	29%	14%	2.4%	4.9%	1.3%	1.8%

The release deviated from linear, with a plateau between 2-8 days, with a substantial release for the 15-day point.

The studies performed with the "spiked" (positive) control samples showed that the recovery of Ag was the lowest at pH 7, which the author attributed to "absorptive losses".

REVIEWER'S COMMENTS:

1. The study does not provide a long-term release pattern for Ag and Cu in this "Ag-Cu Zeolite", since a substantial amount of metal was released by time 15 days (after a plateau of 1 to 8 days) and no sampling was performed after 15-days. The study should have extended beyond 15-days.

2. The data applies only to the particular "Ag-Cu Zeolite" provided by the sponsor. Since it is not clear which specific zeolite is used as the matrix and ion exchange properties vary with zeolite type, the data may not be valid for "Ag-Cu Zeolites" prepared from other zeolites. For this reason, the registrant is being requested to provide further information on the zeolite matrix used in the Ag-Cu Zeolite for which they are seeking registration.
3. The expected predominance of the different Ag and Cu species that can form in the buffer systems should have been calculated and presented as predominance diagrams for both the positive controls and the hydrolysates by using computer programs such as MINTEQ and compared to predominance of Ag and Cu species as a function of pH in the absence of buffers.
4. The detection and quantitation limits of the ICAP system were not clearly specified.
5. Use of pH papers to measure pH is not a desirable method.

Table 1: Sample Weights and pH Values for pH 5 Hydrolysis Samples

SAMPLE	POWDER WT (mg)**	INIT pH	TEST DAY	TEST DATE	FINAL pH
AC-5-8	28.2	5.0	0	5/21	5.0
AC-5-1	33.9	5.0	1	5/22	5.5
AC-5-2	27.8	5.0	2	5/23	5.3
AC-5-3	28.6	5.0	4	5/25	5.5
AC-5-7 (REP)*	34.1	5.0	4	5/25	5.5
AC-5-4	34.7	5.0	8	5/29	5.0
AC-5-5	27.1	5.0	15	6/05	5.0

* REP = Replicate vial also sampled on the same day

** Anhydrous basis (corrected for 20.7% moisture)

Table 2: Hydrolysate Silver and Copper Concentrations for pH 5 Hydrolysis

SAMPLE	TEST DAY	ASSAY DATE	DILUTION	SILVER* PPB	RPD or RSD	COPPER* PPB	RPD or RSD
AC-5-8	0	5/24		105		159	
AC-5-1	1	5/24	1:10	602		951	
AC-5-2	2	5/24		1900	9	2880	5
AC-5-2 (DUP)**	2	5/24	1:10	1730		2740	
AC-5-3	4	5/30		1940	10	3940	9
AC-5-3 (DUP)**	4	5/30	1:10	2350		4620	
AC-5-3 (DUP)**	4	5/30	1:100	2050		3960	
AC-5-7 (REP)**	4	5/30		1370	27	3240	17
AC-5-7 (DUP)**	4	5/30	1:10	1800		3830	
AC-5-4	8	5/30		1690	11	4170	9
AC-5-4 (DUP)**	8	5/30	1:10	2150		4930	
AC-5-4 (DUP)**	8	5/30	1:20	1708		4220	
AC-5-4 (DUP)**	8	5/30	1:10	2110		4960	
AC-5-4 (DUP)**	3	5/30	1:20	1874		4200	
AC-5-5	15	7/02		10100	10	7680	3
AC-5-5 (DUP)**	15	7/02	1:10	9890		7790	
AC-5-5 (DUP)**	15	7/02	1:100	8330		7380	

* Concentrations shown have been corrected for dilution.

RPD (Range Percent Difference) if 2 values; RSD (Relative Standard Deviation) if >2 values.

** DUP = Analysis of replicate aliquot from same vial

REP = Analysis of replicate vial.

Table 3: Silver and Copper Concentrations for pH 5 Hydrolysis, Corrected to Unit Weight

SAMPLE	TEST DAY	ASSAY DATE	SILVER PPB	ug/mg			COPPER PPB	ug/mg		
AC-5-8	0	5/24	105	0.11			109	0.17		
AC-5-1	1	5/24	602	0.53			951	0.84		
AC-5-2 (AVE)*	2	5/24	1815	2.0			2806	3.0		
AC-5-3 (AVE)*	4	5/30	2113	2.2	MEAN	1.8	3940	4.1	MEAN	3.5
AC-5-7 (REP) (AVE)*	4	5/30	1585	1.4	RSD	32 %	3240	2.9	RSD	26 %
AC-5-4 (AVE)*	8	5/30	1906	1.6			4496	3.9		
AC-5-5	15	7/02	9440	10			7617	8.4		

* (AVE) = Value shown is the arithmetic mean of values in Table 2.

Figure 1: Graphical Representation of pH 5 Hydrolysis Results

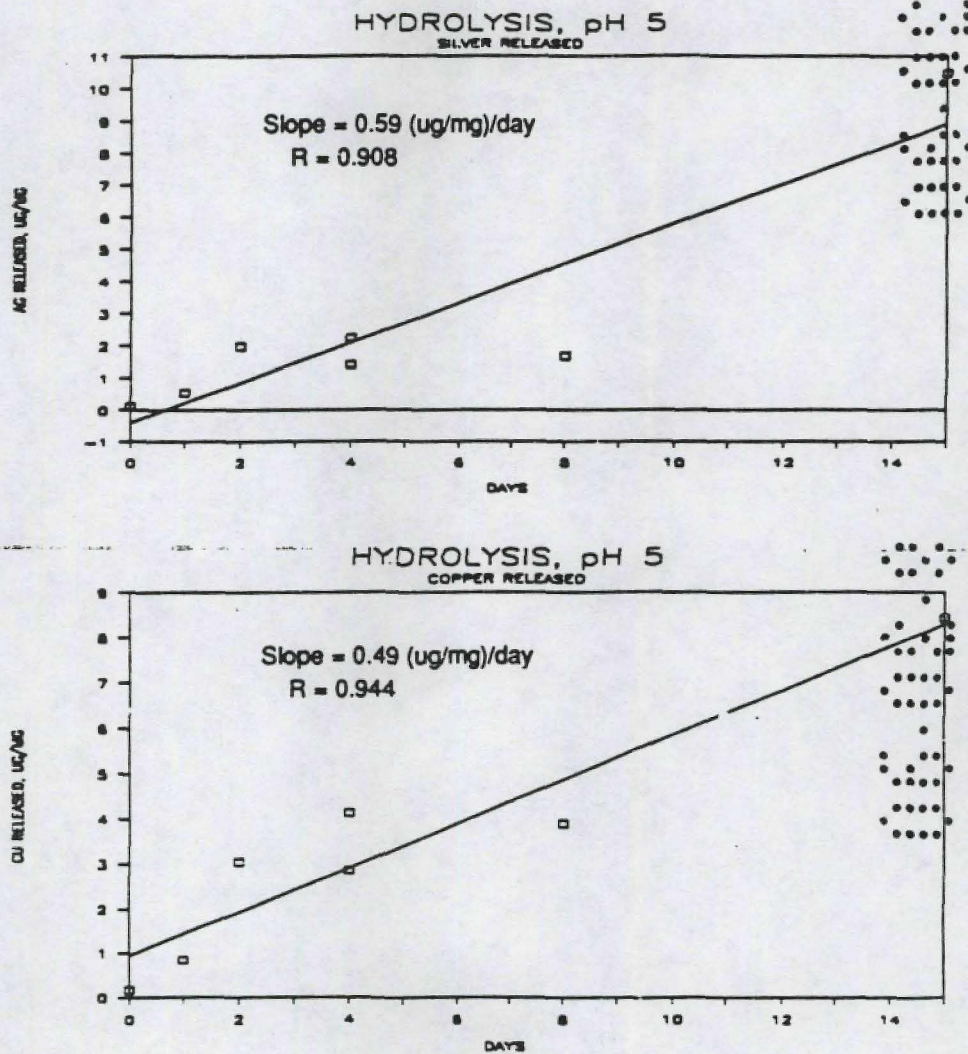


Table 4: Sample Weights and pH Values for pH 7 Hydrolysis Samples

SAMPLE	POWDER WT (mg)*	INIT pH	TEST DAY	TEST DATE	FINAL pH
AC-7-8	25.4	7.0	0	5/03	7.0
AC-7-1	27.0	7.0	1	5/04	6.5
AC-7-2	30.1	7.0	2	5/05	7.0
AC-7-3	26.2	7.0	4	5/07	7.5
AC-7-4	24.6	7.0	8	5/11	6.5
AC-7-5	28.5	7.0	15	5/18	6.0
AC-7-6	23.8	7.0		6/06	7.0
AC-7-7	25.4	7.0		6/06	7.0

* Anhydrous basis (corrected for 20.7% moisture)

Table 5: Hydrolysate Silver and Copper Concentrations for pH 7 Hydrolysis

SAMPLE	TEST DAY	ASSAY DATE	DILUTION	SILVER* PPB	RPD	COPPER* PPB	RPD
AC-7-8	0	5/21		65.8		434	
AC-7-1	1	5/21		78.5		481	
AC-7-2	2	5/21		80.5	16	533	6
AC-7-2 (DUP)**	2	5/24	1:5	94.5		565	
AC-7-3	4	5/21		1060 @	18	602	23
AC-7-3 (DUP)**	4	5/24	1:10	1120 @		755	
AC-7-4	8	5/21		102	6	358	2
AC-7-4 (DUP)**	8	5/21		108		365	
AC-7-5	15	5/21		656	34	2790	5
AC-7-5 (DUP)**	15	5/24	1:10	927		2930	

* Concentrations shown have been corrected for dilution
RPD (Range Percent Difference)

** DUP = Analysis of replicate aliquot from same vial
REP = Analysis of replicate vial.

@ Apparent anomolous result (outlier)

Table 6: Silver and Copper Concentrations for pH 7 Hydrolysis, Corrected to Unit Weight

SAMPLE	TEST DAY	ASSAY DATE	SILVER PPB	ug/mg	COPPER PPB	ug/mg
AC-7-8	0	5/21	66	0.078	434	0.51
AC-7-1	1	5/21	79	0.087	481	0.53
AC-7-2 (AVE)*	2	5/21,24	88	0.087	549	0.55
AC-7-3 (AVE)*	4	5/21,24	1089 @	1.25 @	379	0.78
AC-7-4 (AVE)*	8	5/21	105	0.13	362	0.44
AC-7-5 (AVE)*	15	5/21,24	792	0.83	2860	3.0

* (AVE) = Value shown is the arithmetic mean of values in Table 5.

@ Apparent anomolous result (outlier)

Figure 2: Graphical Representation of pH 7 Hydrolysis Results

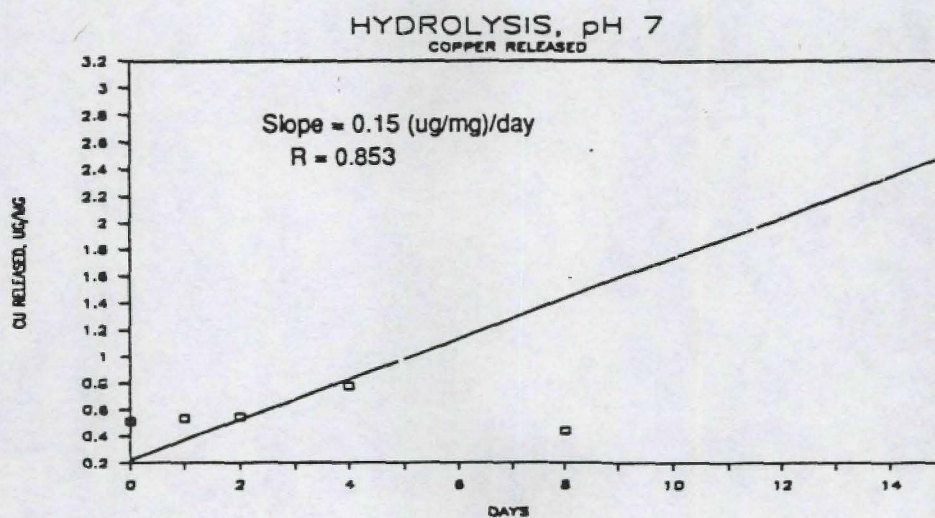
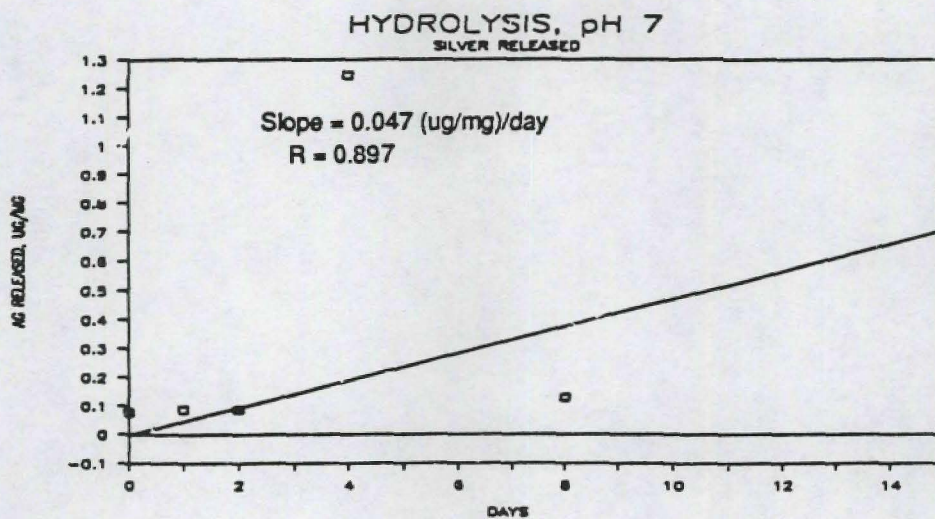


Table 7: Sample Weights and pH Values for pH 9 Hydrolysis Samples

SAMPLE	POWDER WT (mg)**	INIT pH	TEST DAY	TEST DATE	FINAL pH
REPEATS					
AC-9-1R	23.8	9.0	0	6/12	9.0
AC-9-2R	24.5	9.0	1	6/13	9.0
AC-9-3R	29.3	9.0	4	6/16	9.0
AC-9-4R	25.1	9.0	8	6/20	9.0
AC-9-5R	25.5	9.0	15	6/27	9.3

** Anhydrous basis (corrected for 20.7% moisture)

Table 8: Hydrolysate Silver and Copper Concentrations for pH 9 Hydrolysis

SAMPLE	TEST DAY	ASSAY DATE	SILVER PPB	RPD	COPPER PPB	RPD
REPEATS						
AC-9-1R	0	7/02	NA	(Not filtered prior to storage)		
AC-9-2R	1	7/02	138	41	337	14
AC-9-2R (DUP)**	1	7/02	91		293	
AC-9-3R	4	7/02	69		621	
AC-9-4R	8	7/02	65		984	
AC-9-5R	15	7/02	369		930	

** DUP = Analysis of replicate aliquot from same vial

Table 9: Silver and Copper Concentrations for pH 9 Hydrolysis, Corrected to Unit Weight

SAMPLE	TEST DAY	ASSAY DATE	SILVER PPB	ug/mg	COPPER PPB	ug/mg
AC-9-1R	0		Not analyzed		Not analyzed	
AC-9-2R (AVE)*	1	7/02	115	0.14	315	0.39
AC-9-3R	4	7/02	69	0.071	621	0.64
AC-9-4R	8	7/02	65	0.078	984	1.2
AC-9-5R	15	7/02	369	0.43	930	1.1

* (AVE) = Value shown is the arithmetic mean of values shown in Table 8.

Figure 3: Graphical Representation of pH 9 Hydrolysis Results

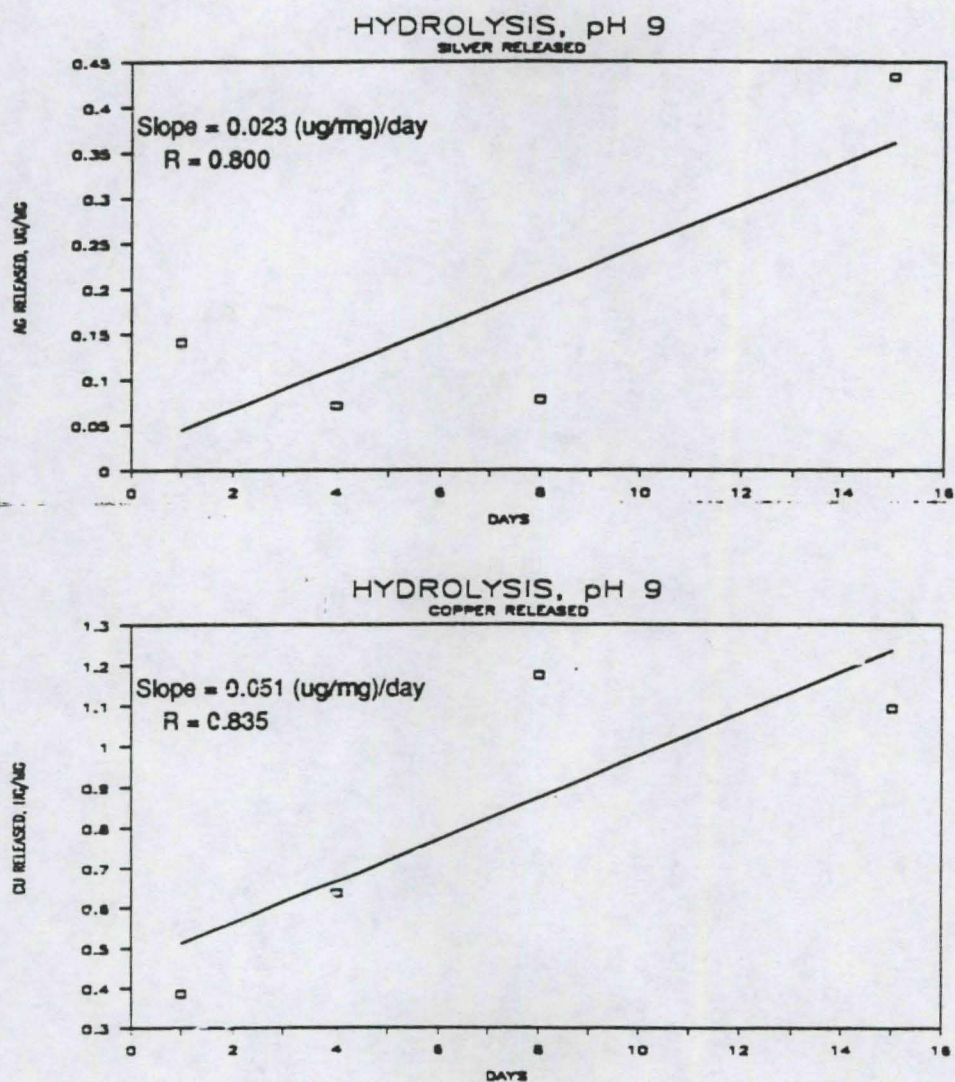


Table 10: Results for Hydrolysis Study Negative Controls (Blanks)

SAMPLE	INIT pH	TEST DAY	TEST DATE	FINAL pH	SILVER PPB*	COPPER PPB*
B-5-8	NR **	0	5/21	5.0	4.7	3.7
B-5-1	NR	1	5/22	5.0	2.4	4.2
B-5-2	NR	2	5/23	5.0	3.9	6.4
B-5-3	NR	4	5/25	5.0	28	19
B-5-4	NR	8	5/29	5.0	ND	ND
B-5-7	NR	8	5/29	5.0	5.0	ND
B-5-5	NR	15	6/05	5.0	6.6	1.3
B-5-6	NR		NA***	NA	NA	NA
MEAN, pH5					7.2	4.9
B-7-8	7.0	0	5/03	7.0	2.3	9.7
B-7-1	7.0	1	5/04	6.5	ND	8.2
B-7-2	7.0	2	5/05	7.0	ND	6.6
B-7-3	7.0	4	5/07	6.5	ND	6.4
B-7-4	7.0	8	5/11	6.5	ND	6.7
B-7-7	7.0	8	5/11	6.5	ND	6.6
B-7-5	7.0	15	5/18	6.5	ND	5.4
B-7-6	7.0		6/06	7.0	NA	NA
MEAN, pH7					0.3	7.1
B-9-8	NR	0	5/21	9.0	1.9	3.6
B-9-1	NR	1	5/22	9.0	2.3	2.8
B-9-2	NR	2	5/23	9.0	2.4	2.0
B-9-3	NR	4	5/25	6.0	13	1.1
B-9-4	NR	8	5/29	6.0	5.9	2.7
B-9-7	NR	8	5/29	6.5	9.3	1.7
B-9-5	NR	15	6/05	7.0	17	3.1
B-9-6	NR		NA	NA	NA	NA
MEAN, pH9					7.4	2.4

* ND = Not Detected (sample response in laboratory blank range); treated as zero in calculating mean.

** NR = Not recorded

*** NA = Not analyzed.

Table 11: Results for Hydrolysis Study Positive Controls (Spikes)

PERCENT RECOVERY

SAMPLE	INIT pH	TEST DAY	TEST DATE	FINAL pH	SILVER %	COPPER %
C-5-8	5.0	0	5/21	5.0	101	110
C-5-1	5.0	1	5/22	5.0	96	109
C-5-2	5.0	2	5/23	5.0	87	106
C-5-3	5.0	4	5/25	5.0	122	110
C-5-3 (DUP)*					122	115
C-5-4	5.0	8	5/29	5.0	92	102
C-5-5	5.0	15	6/05	5.0	115	107
C-5-5 (DUP)*					111	106
C-5-7 (REP)*	5.0	15	6/05	5.0	98	140
C-5-6	NR**		NA**	NA	NA	NA
MEAN, pH 5					105	112
C-7-8	7.0	0	5/03	7.0	80	111
C-7-1	7.0	1	5/04	6.3	70	108
C-7-2	7.0	2	5/05	7.0	77	102
C-7-3	7.0	4	5/07	6.5	75	119
C-7-4	7.0	8	5/11	6.5	72	111
C-7-5	7.0	15	5/18	6.5	64	111
C-7-7 (REP)*	7.0	15	5/18	6.5	54	104
C-7-7 (DUP)*					58	104
C-7-6	7.0		6/06	7.0	NA	NA
MEAN, pH7					69	109
C-9-8	NR	0	5/21	9.0	101	107
C-9-1	9.0	1	5/22	9.0	110	109
C-9-2	9.0	2	5/23	9.0	61	105
C-9-3	9.0	4	5/25	6.5	100	103
C-9-4	9.0	8	5/29	6.0	65	106
C-9-5	9.0	15	6/05	7.0	83	97
C-9-7 (REP)*	9.0	15	6/05	7.0	132	101
C-9-7 (DUP)*					136	101
C-9-6	NR		NA	NA	NA	NA
MEAN, pH9					99	104

* (DUP) = Analysis of replicate sample from same vial
 (REP) = Analysis of replicate vial

** NR = Not recorded
 NA = Not analyzed

Page 12 of 66

Arthur D Little

1.18

Figure 4: Comparison of pH 5, 7, and 9 Results for Silver

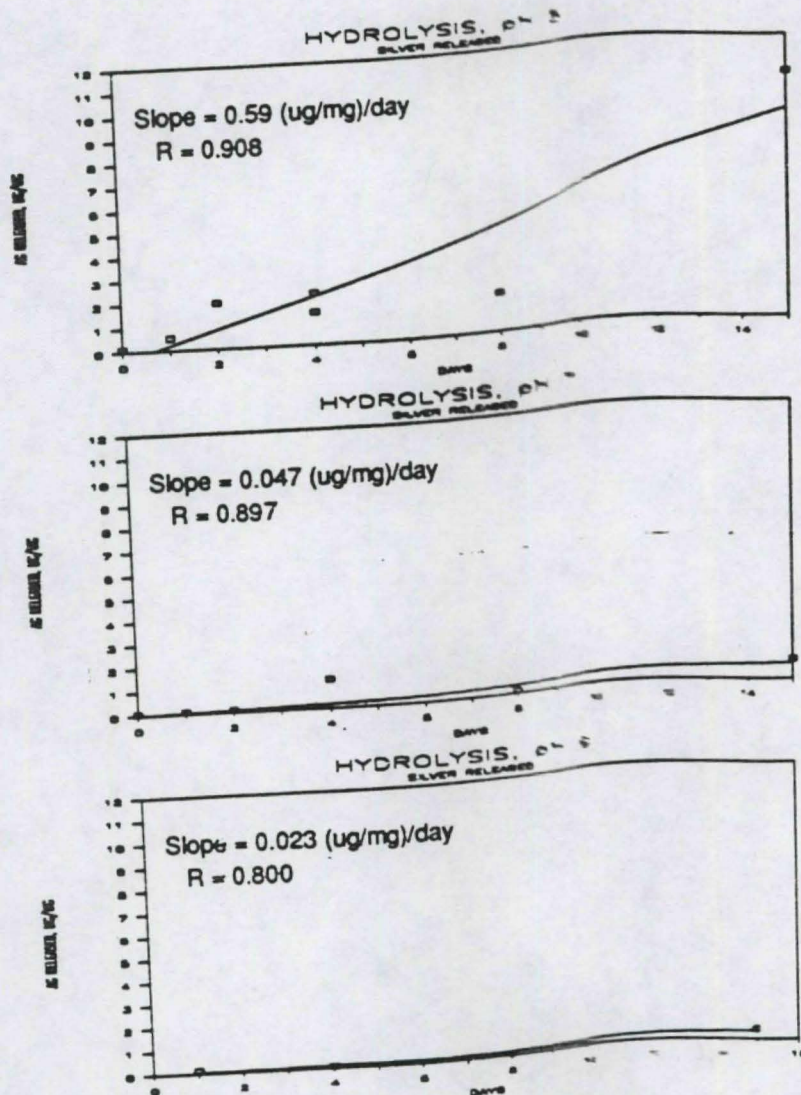


Figure 5: Comparison of pH 5, 7, and 9 Results for Copper

